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## Air Force Office of Scientific Research

# **Annual Technical Progress Report**

**Durability Characterization of POSS-based Polyimides and Carbon-Fiber Composites for Air Force-Related Applications** 

## 31 December 2007

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# Durability Characterization of POSS-based Polyimides and Carbon-Fiber Composites for Air Force-Related Applications

Andre Lee, Michigan State University

# Overall Objective

The objective of this study is to expand the performance space of carbon-fiber reinforced polyimide composites using a synergistic combination of hybrid inorganic-organic, nano-structured chemicals and state-of-the-art oligoimide chemistry. In particular, this study will formulate hybrid, nano-structured polyimide composites, from the molecular to the macroscopic level, while tailoring their properties to the service durability requirements of Air Force-related applications.

# Status of Final Report

This research program aims to explore the use of hybrid inorganic-organic, nanostructured chemicals in second-generation, high-performance thermosetting polyimide resins and carbon-fiber reinforced polymeric matrix composites is proposed. This work builds on the progress made in the past several years, which has enabled the use of nano-structured chemical approaches through materials engineering principles to make significant performance enhancements on many difficult-to-attend and yet desirable properties of conventional organic thermosetting polyimides and their composites by incorporate nano-structured chemicals such as Polyhedral Oligomeric Silsesquioxane (POSS). This nano-structured chemical "reinforcement" approach not only retains the light-weight nature of organic polymers, but also substantially improves many other desirable performance qualities, i.e., high temperature mechanical properties and oxidative stability, surface durability, etc., in comparison to conventional organic polymers. The three-dimensional nature and nanoscopic size of POSS are the key contributors to the material property improvements observed through POSS incorporation. In the past 35 months, we explored two approaches to modify thermosetting polyimide resins. It was found that the incorporation of well-dispersed, nano-structured chemicals will benefit the high temperature durability of polyimide matrix composites. Moreover, the addition of cage-like, multi-functional phenylethynyl phthalic imide POSS exhibited multiple benefits in performance, durability as well as processing of thermosetting polyimides to carbon-fiber composites.

# **Background**

The field of hybrid organic-inorganic materials has grown drastically over the last several years. This interest stems from the fact that our ever increasing ability to custom-build and control molecular structure at several length scales, thereby developing materials with new unique properties. This ability to control both composition and structure of hybrid materials at varying length scales is sometimes broadly referred to as nano-composite systems. One class of organic-inorganic nano-structured material is Polyhedral Oilgomeric Silsequioxanes (POSS). The hybrid (organic/inorganic) composition of POSS technology enables it to occupy a very unique and dramatically enhanced property space relative to traditional hydrocarbons and inorganic materials (Figure 1). An important benefit is that it affords the material formulations of Nano-structured Chemicals with excellent thermal and oxidative stability. This is largely due to the inorganic component.

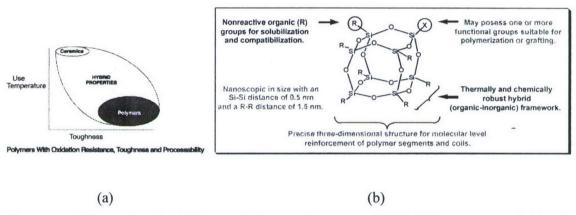


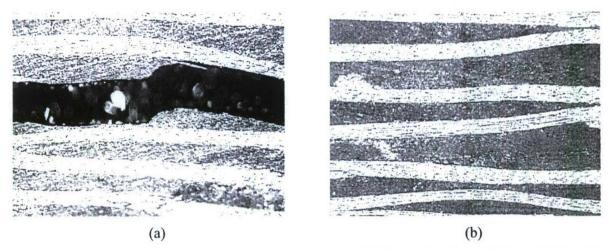
Figure 1. (a) The unique hybrid (organic-inorganic) nature of POSS Nano-structured Chemicals. (b) The anatomy of a POSS chemical.

To fulfill the ever increasing performance requirements in the highly demanding aerospace environments while preserving the structure-to-weight ratio, there is a continue interest for the development of high-performance thermosetting resins and their carbon-fiber reinforcement composites. Currently, high temperature thermosetting polyimide resins such as AFR-PE4 and its composites are been evaluated for applications at temperature as high as 400°C, with potential uses in spacecraft structures. In space application, it was known the addition of Si can improve atomic oxygen (AO) erosion of polymeric materials. Therefore, the incorporation of structural Si such as POSS can expect to have a significant benefit of AFR-PE4 like carbon-fiber composites.

#### Significant Findings in Year 1 (2005)

In year 1, we explore two possible approaches to incorporate POSS moieties into a class of phenyl-ethynyl terminated oligoimide, PETI, resins and the feasibility of these approaches for fabrication of continuous fiber reinforced composites. It was concluded that the most effective approach to improve performance is the addition of POSS with multi-function, reactive oligoimide, similar to that of end-capper used in convention organic, reactive oligoimide. This is evident with the composite panel made with oigoimide resin containing 3 wt% of POSS-PETI, as

shown in Figure 1 (a) and (b). *Upon exposure to 450°C while under load*, we observed no cracks for composites containing "POSS-PETI", while significant cracks occurred for the control composite panel containing no POSS.



**Figure 1.** (a) The control composite sample under going DMA testing from 25°C to 450°C with a heating rate of 2°C per minutes. (b) 3 wt% "POSS-PETI POSS" was added to conventional organic oligoimide resin in T650-35 composite sample under going identical thermal mechanical cycle as the control.

As a part of this effort we also evaluate the TOS of the matrix materials using conventional TGA method. In Figure 2, we compared the percent weight remaining versus temperature of POSS-PETI with current HFPE-II-52 resin. As see from Figure 2, at 90% weight, an improvement of more than 50°C was observed.

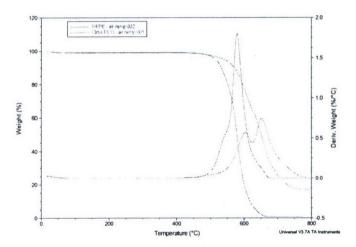


Figure 2. Thermogravimetric analysis (TGA) of POSS-PETI and HFPE-II-52, with heating rate of 10°C/min under constant flow of dry air. The red trace was POSS-PETI and the green trace is HFPE-II-52. The change in weight with temperature was also plotted for clarity.

During the annual program review (August 2005), it was point-out by a researcher (Dr. Timothy Haddad) at the AFRL-PRSM that the cage structure for the initial aminophenyl POSS may not be intact based on the lack of resonance peak in liquid <sup>29</sup>NMR analysis. It was known for thermoplastic polymers (non-crosslinked) containing POSS, that cage structure is important in improving thermal stability of POSS copolymer. Therefore, an effort to investigate the influence of POSS cage structure on TOS performance for highly crosslinked thermoset materials was initiated.

# Significant Findings in Year 2 (2006)

In year 2, we explore different synthesis approaches to preparation of functionalized POSS frameworks. In general, there are two approaches to prepare functionalized POSS. First approach, the organic groups (or existing functional groups) on an existing POSS framework are simply functionalized (or transformed) using traditional organic synthesis. A second approach involves the direct synthesis of functionalized POSS cages from silicon based starting materials. Generally this approach involves the hydrolytic condensation of trifunctional organosilanes (R-SiX<sub>3</sub>) and may occur under either acidic or basic conditions. In the first approach, the stability of Si-O core is generally assumed. Therefore, if one begins with a monodisperse Si-O framework (e.g. an octamer) the product will and should retain the same monodisperse Si-O framework. For the direct synthesis of functionalized POSS approach, however, depending on synthetic conditions a variety of silsesquioxane structures are possible including completely and incomplety condensed Si-O structures. Although each reaction can be different from another, yet, with proper selection of reagents and solvents a high degree of selectivity can be achieved.

To prepare aminophenyl substituted POSS, based on the first approach which describes synthetic procedures for exclusively from organic chemistry modification of existing POSS frameworks. Typically, these involve the aromatic nitration of phenyl bearing POSS monomers such as octaphenyl POSS and dodecaphenyl POSS followed by reduction of the nitro group to an amine. While this approach has the theoretical benefit of retaining the cage structure, the nitration of the aromatic rings is nonselective and leads to the formation of meta, para, and ortho positional isomers. The processibility and thermo-oxidative stability are generally known to depending on isomeric states and their distribution, which can in turn affect the performance composites made with these POSS materials. Furthermore, careful examination of published literature and our own investigation on the so-called octa(aminophenyl) POSS as prepared by nitration/reduction of octaphenyl POSS using <sup>29</sup>Si NMR technique lead us to believe that the theoretical benefit of retaining the cage structure assumption may not necessary be correct.

A second approach is the direct approach starting from the specified isomer of aminophenyltrimethoxysilanes and using acid or base catalysis. Our initial efforts involved acid catalysis using the conditions similar to that reported for the synthesis of octa(aminopropyl)POSS. While this approach was successful in obtaining cage-like aminophenyl POSS, the product isolated as an anilinium salt which was undesirable. Therefore base catalysis approach is used for scale-up synthesis.

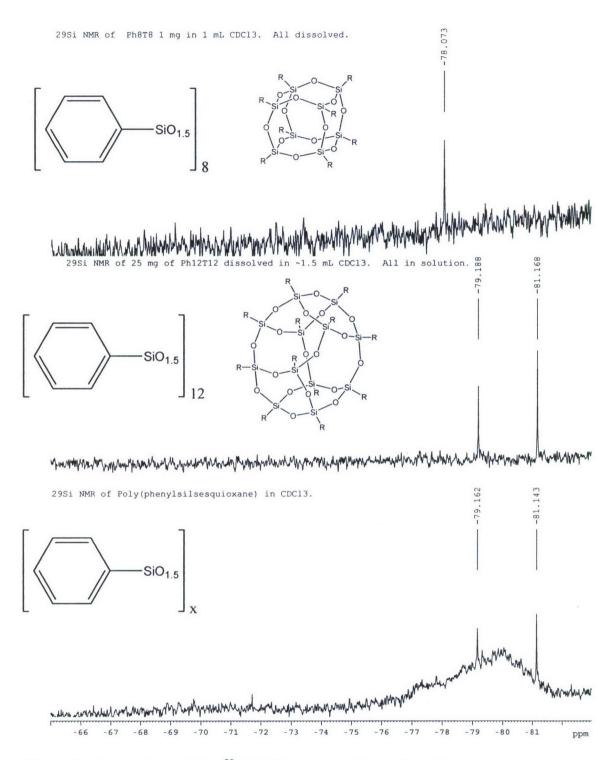
Synthesis of Phenylethynyl phthalimide from aminophenyl silsesquioxanes: There are several approaches reported to obtain phathalimide from model reaction between aniline and phathalic anhydride. Due to our eventual used of this compound in carbon-fiber reinforced polymer matrix composites, the following method was used. In a torch-dried 100 ml round-bottom flask, fitted with a condenser, methanol (5 ml) was added to 4-PEPA (4.0 g, 16.1 mmol).

The mixture was magnetically stirred at about 50°C under nitrogen purge. After about 1.5 hours, the phathalic anhydride was converted to phathalic acid, methyl ester (4-PEPE), which was completely soluble in methanol and forms a light-yellow solution with no observable solid matter. This solution was then stirred for additional 30 minutes, prior to adding 16.1 mmol (2.335 g) of aminophenyl silsesquioxaes. A dark-color solution was form instantaneously, indicating a rapid formation of phathalic amic acid. After continuous stirring for another 20 minutes, the phathalic amic acid solution was poured into to a glass bottle and heated to the boiling temperature of methanol on a hot plate with a magnetic stir for additional 10 minutes. The solution was first allowed to cool to room temperature and then placed into a mechanical-conversation oven. The oven was heated from RT to 200°C with a ramp-rate of 5°C/min and hold at 200°C for 2 hours, heated to 240°C with same ramp rate and hold at 240°C for 1 hour. A brown-colored powder was obtained. According to NMR analysis, the powder was phenylethynyl phthalimide silsesquioxane, and the silsesquioxane structure was not altered with this synthesis procedure.

Solution <sup>29</sup>Si NMR Spectroscopy Analysis: It is well established that the solution <sup>29</sup>Si NMR spectroscopy is an excellent tool for revealing the structural environment of silicon containing materials. For silsesquioxanes, the spectra of well-defined oligomeric cages contain sharp resonances with half-peak widths on the order of 1 or 2 hertz, while the spectra of ill-defined silsesquioxane "resin" is broad and uninformative due to a myriad of chemical environments present. For example, in the top trace of Figure 3, the <sup>29</sup>Si spectrum of octaphenylsilsesquioxane,  $(C_6H_5)_8Si_8O_{12}$ , reveals a single sharp resonance 2 hertz wide as all eight silicons are chemically identical. The second trace in Figure 3 shows the spectrum of dodecaphenylsilsesquioxane,  $(C_6H_5)_{12}Si_{12}O_{18}$ , a single pure compound with two chemical environments and thus just two sharp resonances a few hertz in width shifted a few ppm from their  $(C_6H_5)_8Si_8O_{12}$  cousin. The bottom trace is of ill-defined polyphenylsilsesquioxane that contains a small amount of  $(C_6H_5)_{12}Si_{12}O_{18}$ . The bulk of the material has so many different chemical environments for all the silicon atoms present that the spectra shows a broad hump of

peaks running into each other, extending from approximately -76 to -82 ppm.

It is reported in the literature that octaphenylsilsesquixoane, (C<sub>6</sub>H<sub>5</sub>)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>, is converted mixture of meta-, ortho-, and para-substituted into isomeric 60:30:10 octanitrophenylsilsesquixoane, (NO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>, and that this compound can be reduced to an isomeric mixture of meta- ortho- and para-substituted octaaminophenylsilsesquioxane, (NH<sub>2</sub> C<sub>6</sub>H<sub>5</sub>)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>. Solution <sup>29</sup>Silicon NMR spectra of these materials are shown in Figure 4. The top trace shows the product from the nitration of octaphenylsilsesquioxane. Two main environments are clearly visible centered at -79 and -83 ppm. The <sup>1</sup>H NMR spectrum reveals that each phenyl ring has but one nitro group on it; with three isomeric positions possible on each phenyl ring, a number of structural octanitrophenylsilsesquioxane isomers are possible. This would explain the large number of sharp lines observed, and thus it is not unreasonable to assume that the compound consists of an isomeric mixture of T<sub>8</sub> cages. After this material is reduced to an amine, the <sup>29</sup>Si spectrum is suddenly much broader than is reasonable for just T<sub>8</sub> isomers to be present. It is far more likely to suggest that the octameric cage structure is no longer intact, and that under the synthesis conditions, the cage was opened and redistributed into a structurally illdefined resin. Note that the breadth of the signals from -75 to -82 ppm is similar in size to that observed for polyphenylsilsesquioxane resin. For comparison, the bottom trace in Figure 4, shows the <sup>29</sup>Si NMR spectrum of a meta-aminophenylsilsesquioxane cage mixture, that probably also has a small amount of poorly-defined resin present.



**Figure 3.** Comparison of the <sup>29</sup>Si NMR spectra of octaphenylsilsesquioxnae (upper trace), dodecaphenylsilsesquioxane (middle trace), and ill-defined silsesquioxane resin containing a small amount of the dodecaphenylsilsesquioxane (lower trace).

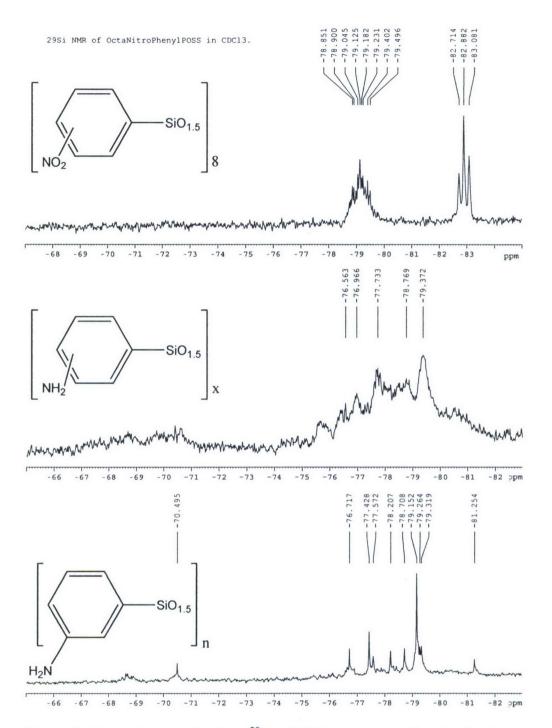
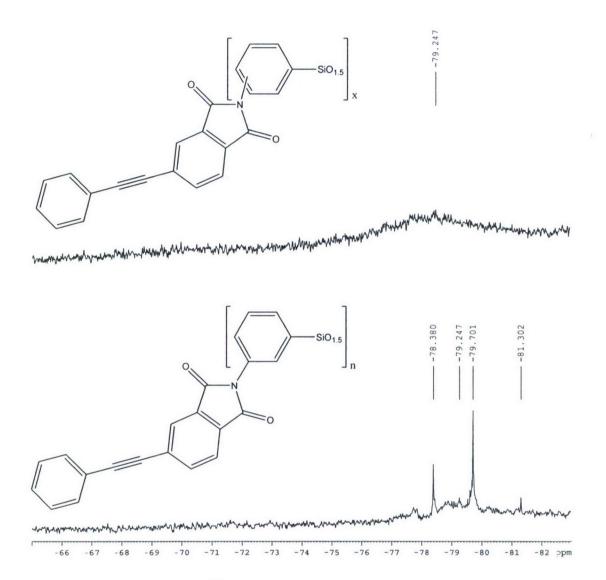


Figure 4. Comparison of the <sup>29</sup>Si NMR spectra of mixed isomers of octanitrophenylsilsesquioxane obtained by nitration of octaphenylsilsesquioxane (upper spectrum), the product obtained by reduction of octanitrophenylsilsesquioxane (middle spectrum), and a cage mixture of meta-aminophenylsilsesquioxane obtained by the base assisted condensation of meta-aminophenyltrimethoxy silane (lower spectrum).



**Figure 5.** Comparison of the <sup>29</sup>Si NMR spectra of the imidization derivatives obtained from structurally undefined aminophenyl silsesquioxane (upper trace), and that obtained from a cage mixture of meta-aminophenylsilsesquioxane (lower trace).

Figure 5 compares the 29Si NMR spectra of the phenylethynyl phthalicimide silsesquioxane resin (top trace) and cage mixture (lower trace). Since there is no significant change observed as compare to traces shown in Figure 4, it can be concluded that the aniline/anhydride reaction has very little effect on the cage structure and its distribution.

Thermal and Thermo-oxidative Stability of differentvAminophenyl silsesquioxanes (APS's): Thermogravimetric analysis (TGA) using constant heating-rate, under a constant flow-rate of nitrogen or air as supplied by high pressure gas cylinder, we compared thermal and thermo-oxidative stability of silsesquioxane of different structures, respectively. The traces of

percent weight remaining (wt%) versus temperature of all three structures of APS under constant flow-rate of nitrogen and air were shown in Figure 7 (a) and (b), respectively. At temperatures between 100°C and 150°C, regardless with the type of gas used, the resin-like APS exhibited a first step-wise drop in its weight. In the nitrogen environment, Figure 7(a), the m-APSC show the first step-wise drop at a onset temperature of around 550°C, the p-APCS show the first step-wise drop at around 500°C, and resin-like APS show a second step-wise drop at around 400°C. Here, we were somewhat surprise that m-APCS has a better thermal performance than p-APCS, however, this observation maybe related to the additional isomeric flexibility attributed to the meta-functionality. In the air environment as shown in Figure 7(b), the m-APCS also exhibited a superior thermo-oxidative stability over the other two aminophenyl silsesquioxanes. In Figure 7(c), we compare conventional HFPE-II-52 with HFPE-II-52 modified with 3 wt % of resin-like POSS-PETI and cage-like POSS-PETI, respectively. It is clear from the TGA traces, addition of cage-like POSS-PETI offers the highest performance of thermo-oxidative stability to the conventional, organic HFPE-II-52 polyimide matrix.

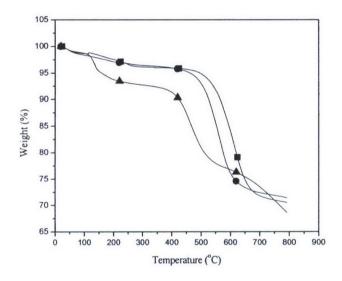


Figure 7 (a). Thermogravimetric analysis (TGA) of different aminophenyl silsesquioxanes. The heating rate was  $10^{\circ}$ C/min under constant flow of N<sub>2</sub>. The solid line with represents meta-aminophenylsilsesquioxane cage mixture  $(m-NH_2C_6H_5[SiO_{1.5}])_n$  where n=8,10,12; dash with represents para-aminophenylsilsesquioxane cage mixture  $(p-NH_2C_6H_5[SiO_{1.5}])_n$ ; and dash-dot with represents OAPS from the resin-like aminophenylsislesquioxane.

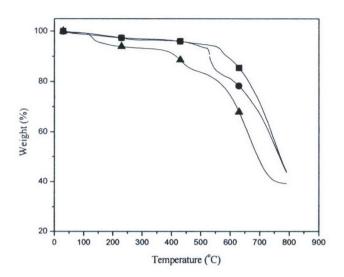
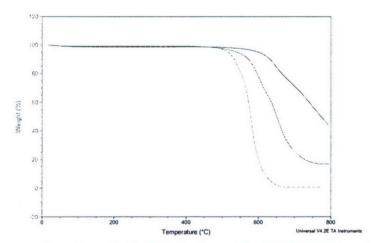


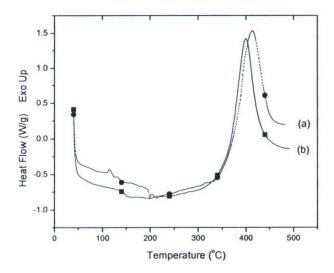
Figure 7 (b). Thermogravimetric analysis (TGA) of different aminophenyl silsesquioxanes. The heating rate was  $10^{\circ}$ C/min under constant flow of air. The solid line with  $\blacksquare$  represents meta-aminophenylsilsesquioxane cage mixture  $(m-NH_2C_6H_5[SiO_{1.5}])_n$  where n=8,10,12; dash with  $\blacksquare$  represents para-aminophenylsilsesquioxane cage mixture  $(p-NH_2C_6H_5[SiO_{1.5}])_n$ ; and dash-dot with  $\blacksquare$  represents Resin-like APS.



**Figure 7 (c).** Thermogravimetric analysis (TGA) of cage-like POSS-PETI, resin-like POSS-PETI, and HFPE-II-52, with heating rate of 10°C/min under constant flow of dry air. The red trace is the conventional HFPE-II-52, the green trace is HFPE-II-52 modified with 3 wt% of resin-like POSS-PETI, and the blue trace is HFPE-II-52 modified with 3 wt% of cage-like POSS-PETI.

Curing kinetics of Phenylethynyl phthalimide Silsesquioxanes: In Figure 8, we depicted DSC traces of phenylethynyl phthalimide silsesquioxanes as derived from  $(m-APSC)_n$  and Mayaterial's OAPS. In the figure legend, these silsesquioxanes were referred as meta-PETI and

Laine-PETI, respectively. These traces clearly demonstrated that reaction of the ethynyl group in these silsesquioxanes began at around 330°C, with peak temperature at around 400°C and the integrated heat of reaction was around 270 J/g (or 96 KJ per mole of ethynyl group). These results were similar to other high temperature oligoimide resins end-capped with phenylethynyl phthalimide, which suggest that the Si-O core did not hinder the crosslinking reactions of ethynyl group at all. Hence makes these phenylethynyl phthalimide silsesquioxanes as excellent additives to other high temperature organic PETI oligoimide resins for improved thermooxidative stability as desired in many applications involving carbon-fiber reinforced polymer matrix composites. As we compare only these two DSC traces, it was observed the peak temperature for meta-PETI is about 11°C lower than Laine-PETI and the width of exothermic peak is narrower for meta-PETI than Laine-PETI. These observations further support the NMR analysis that meta-PETI contains mostly cage-like structure, while Laine-PETI contains more resin-like structure of silsesquioxanes. In addition, meta-PETI exhibited a clear Tg at around 150°C, while T<sub>g</sub> for Laine-PETI is around 200°C. Results for DSC further confirm WXRD observation that both silsesquioxanes contains no significant degree of crystallinity. Therefore these two silsesquioxanes exhibit liquid-like behavior at temperatures above Tg prior to any significant ethynyl crosslinking.



**Figure 8.** Differential Scanning Calorimetry (DSC) analysis of curing of Phenylethynyl phthalimide derived from (a) OAPS from Mayaterials; and (b) meta-aminophenylsilsesquioxane cage mixture  $(m-NH_2C_6H_5[SiO_{1.5}])_n$  where n=8,10,12. The heat rate was  $10^{\circ}$ C/min.

# Significant Findings in Year 3 (2007)

## Mechanical aging data:

Significant effort in generating high temperature mechanical data (550°F and 600°F) of carbonfiber composites exposed to different extent of aging at elevated temperature was the focus on year 3. These mechanical data on composites further confirm the improved thermooxidative stability due to addition of POSS nano-structured chemicals.

## Addition of POSS-trisilanols

In the following two Tables, we show the % weight lost and the residual mechanical data after 1024 hours of exposure at 550°F.

**Table 1.** Percent weight lost data for composite panels aged at 550°F air oven.

Sample (~ 60vol% T650-35 Carbon Fabrics)	Weight Lost after 524 hours at 550°F	Weight Lost after 1024 hours at 550°F
HFPE-II-52	0.66 %	0.90 %
+7.5% Phenyl Triols	0.60 %	0.84 %
+7.5% Ethyl Triols	0.54 %	0.81 %
+15% Phenyl Triols	0.37 %	0.60 %
+15% Ethyl Triols	0.68 %	0.90 %

**Table 2.** Residual mechanical performance of composites after aged at 550°F for 1024 hours in an air oven. Flexural test was conducted at 550°F and average value was determined using five samples.

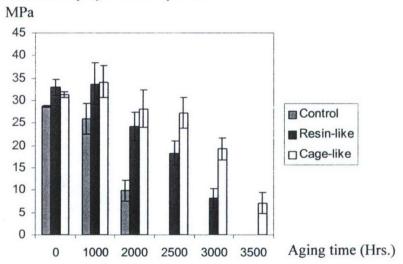
Sample (~ 60vol% T650-35 Carbon Fabrics)	Flexural Strength (Ksi)	Flexural Modulus (Msi)
HFPE-II-52 (Control)	94.9 ± 6	$7.8 \pm 0.13$
with 7% POSS-Phenyl Triol	100.7 ± 3	$8.3 \pm 0.14$
with 7% POSS-Ethyl Triol	95.7 ± 8	8.5 ± 0.16
with 15% POSS-Phenyl Triol	108.2 ± 5	$8.6 \pm 0.14$
with 15% POSS-Ethyl Triol	100.6 ± 8	8.4 ± 0.17

Results from Tables 1 and 2 showed the addition of Ph-POSS trisilanol in HFPE-II-52 can reduce the amounts of weight lost for long dwell at elevated temperature. As a consequence, the residual mechanical performance of Ph-POSS trisilanol containing HFPE-II-52 composite is better than the control sample. Although the improvement on thermo-oxidative stability using Et-POSS trisilanol is less than the addition of Ph-POSS trisilanol, but in general, we have clearly demonstrated the addition of POSS will improve thermo-oxidative stability of the matrix materials and leads to an improved performance in composites.

# Addition of PETI functional silsesquioxanes (PETI-POSS)

Six 8 ply thick 10" by 10" carbon-fiber (T650) composite panels were fabricated to obtain required composite test coupons for thermo-oxidative stability (TOS) testing and fatigue testing. The resin contain of all these composite panels was about 35 wt%. For TOS testing, it was selected to evaluate the residual interlaminate shear strength at 315°C (600°F), after exposed the test coupons in a circulated air oven with temperature set at 315°C for a know period of time. After 2000 hours of exposure, the strength of control composite coupon had drop from the initial value of around 28 MPa to 9 MPa, while composite containing 6 wt% of cage-like PEPI POSS in matrix exhibited a significant TOS. The strength for composite made with POSS-modified polyimide matrix show a change from 31 MPa to 28 MPa. These test coupons did not show any significant changes in the interlaminate shear strength until 3500 hours of aging time at 315°C. Although the crosslink density of HFPE-II-52 with PETI-POSS additions is expected to increase as compared to the control, but throughout the entire evaluation period, we did not observed any significant reduction in the fracture strength. In addition, the T650 carbon fiber used in this study is that of conventional high sizing, the adhesion between matrix and the T650 carbon fiber did not seem to be affected by the inclusion of PEPI-POSS.

Figure 9 show results of interlaminate shear strength measured at 600°F as a function of exposure time in a 600°F air-flow oven. It is clear the addition of cage-like PETI-POSS is most effective in improving TOS of polyimide composites.



#### **Summary**

In the 35 months, this research project funded by AFOSR has focused on exploring various POSS chemical schemes for use in high-performance, high-temperature oligoimides, processibility of these POSS-oligoimide resins as the matrix material for continuous carbon fiber-reinforced composites and the resulting thermo-oxidative stability (TOS) of these hybrid polymer matrix composites for Air Force-related applications. Results of this work demonstrated the general performance enhancements due to addition of POSS. It was also found that the extent of performance enhancement in resins as well as composites depend on the molecular architecture of POSS while using identical organic oligoimide resins. It is worthwhile to mention that the processibility of POSS and POSS modified hybrid oligoimide resins is also depending

on the molecular architecture of the nano-structured chemicals, which may improve the manufacturing of thermosetting polyimide composites by providing a more appropriate selection of POSS additives.

A more fundamental effort is underway to explore possible mechanisms leading to the observed performance enhancements in resins and composites as influenced by the POSS chemistry as well as the molecular architecture of nano-structured chemicals. Understanding these fundamentals is critical in developing a systemic approach that will best achieve the synergistic benefits between various nano-structured chemicals, the chemistry of the host organic polymers, and the chemistry of the reinforcing fiber to meet the future challenges of Air force composite applications. The effort will utilize a broad range of experimental methods including materials synthesis, chemical spectroscopic analysis (FT-IR, Raman spectroscopy, NMR, XPS, GPC, etc.), morphological analysis (X-ray scattering, electron microscopy, optical microscopy, dynamic mechanical spectroscopy, rheology, etc.), mechanical characterization (static and fatigue, fracture, etc.) and thermal analysis.

# **Personnel Supported**

Dr. Andre Lee, Principal Investigator.

Dr. Kausik Mukhopadhyay; Dr. Zhiyi Bao, Dr. Daniel Drazkowski, (Postdoctoral Fellows) Mr. Daniel Drazkowski (Completed his Ph.D. in April 2007), Ms. Ping Liu (completed her Ph.D. in June 2007), Mr. Yining Xia

### **Publications**

Andre Lee and Sandi Campbell, "Effect of POSS Trisilanols on 6F Polyimides with Phenylethynyl endcap Composite Applications", Accepted by High Performance Polymers. Andre Lee, Timothy Haddad and Joseph Schwab, "Molecular Structure Analysis of Aminophenyl Silsesquioxanes", Accepted for Publication in Chemistry of Materials Andre Lee and Daniel Drazkowski, "High Temperature Performance of POSS-Polyimide Composites", to be submitted Daniel Drazkowski, Ph.D. Thesis

#### Interactions/Transitions

Attended High-Temple 2005 meeting at Point Clear, AL. Presented a talk entitle "Nano-Structure Chemicals Modified 6F-Polyimides Carbon Fiber Composites".

Attended High-Temple 2006 meeting.

Attended High-Temple 2007 meeting at Sedona, AZ. Presented a talk entitle "Development of POSS-PETI for High Temperature Carbon-Fiber Composites"

Attended SAMPE 2006 meeting at Long Beach, CA.

Attended 232<sup>nd</sup> ACS National meeting at San Francisco, CA.

Attended SAMPE 2007 meeting at Baltimore, MD

Assist AFRL-PRSM in the development of POSS aniline. Evaluate atomic oxygen (AO) resistance on POSS-containing 6F polyimide composites.

#### New Discoveries/Inventions/Patent Disclosures

Hybridplastic Inc. agree to scale-up manufacturing of cage-like aminophenyl POSS